Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen (ITM Syngas)

DE-FC26-97FT96052

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Objectives
ITM Syngas Ceramic Membrane Reactor Technology

- **Develop technology for the low-cost conversion of natural gas to hydrogen and synthesis gas**
  - **Lower hydrogen production costs will facilitate the transition to a Hydrogen Economy**
- **Scale-up through three levels of pilot-scale testing and precommercial demonstration**
- **Obtain data necessary for the final step to full commercialization of the ITM Syngas technology**

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Project Budget

Funding ($000's)	FY2003	FY2004	anticipated FY2005
DOE-Fossil Energy	4,560	3,648	4,000
DOE-Energy Efficiency	1,300	200	0
Industry	7,460	4,897	5,090
Total	13,320	8,745	9,090

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Technical Barriers and Targets
Hydrogen Production *

- DOE Technical Barriers
  - Fuel Processor Capital Costs (A)
  - Carbon Dioxide Emissions (D)
  - Oxygen Separation Technology (AA)
- DOE Technical Targets
  - For 2005
    - Reforming: $1.98/kg H_2, 72% efficiency
    - Total: $3.00/kg H_2
  - For 2010
    - Reforming: $0.82/kg H_2, 75% efficiency
    - Total: $1.50/kg H_2

* June 2003 Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Program Plan

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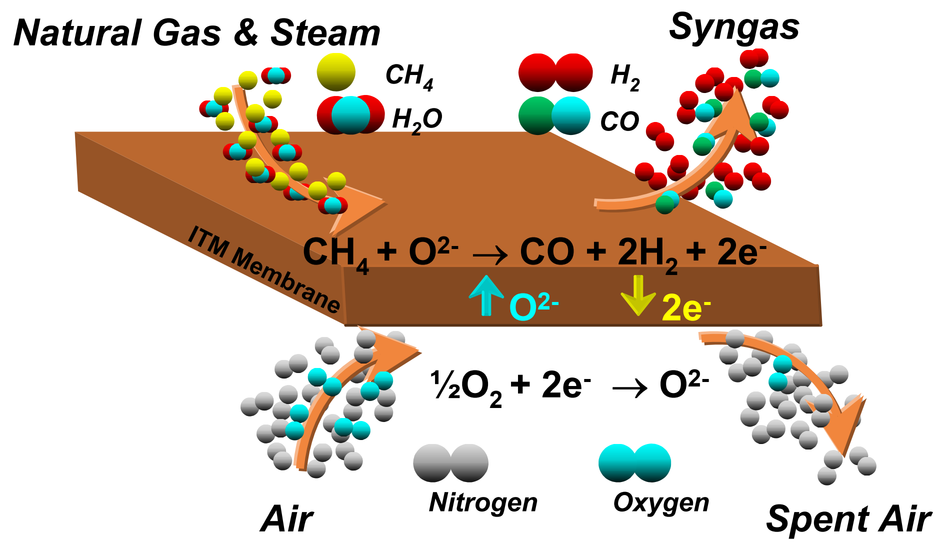
Approach

- Ion Transport Membranes (ITM)
  - Non-porous multi-component ceramic membranes
  - High oxygen flux and high selectivity for oxygen
  - Operate at high temperatures, typically over 700 °C



- ITM Syngas combines air separation and methane partial oxidation into a single unit operation, resulting in significant cost savings
- Key technology aspects addressed in this project
  - Develop membrane and reactor designs, membrane materials, and ceramic fabrication methods
  - Obtain membrane performance test data for scaleup and commercialization

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Project Safety

- Methodology and Techniques
  - Technical Risk Review to evaluate step-outs and plan fallback solutions
  - Design safety review, including Hazard and Operability analysis (HAZOP)
  - Operational Readiness Inspection prior to start of test
  - Management of Change review for equipment and procedures
- Design Approach
  - Conventional plant design for high temperature and high pressure syngas processes
  - Automated control systems for interlocks, alarms, and shutdowns
    - Unattended operation of experiments
  - Active and passive designs to address module leakage and reactor operation

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Project Timeline

Oct'97-Apr'00	May'00-Sep'07		Oct'07-Dec'09
Phase 1	Phase 2	Phase 2 extension	Phase 3
1 2 3	4 5 6 ↑	7 8	9 10

Phase 1 Material and membrane development	1. **Identified family of high-pressure membrane materials** 2. **Verified ceramic-to-metal seal performance** 3. **Selected planar membrane over tubular design**
Phase 2 Scaleup to pilot-scale reactors (extension needed to meet all Phase 2 objectives)	4. **Demonstrated stable membrane performance at elevated pressure for over 6 months** 5. **Tested pilot-scale planar membrane module in 24,000 SCFD* Process Development Unit (PDU)** 6. **Demonstrated target performance of pilot-scale membrane** → 7. **Test commercial-size membrane** 8. **Start operation of 330,000 SCFD Sub-scale Engineering Prototype (SEP) with commercial-size membranes**
Phase 3 Scaleup to pre-commercial demonstration	9. **Start operation of 15 million SCFD Pre-Commercial Technology Demonstration Unit (PCTDU)** 10. **Update process economics and launch commercialization**

* std. cu. ft. per day of synthesis gas

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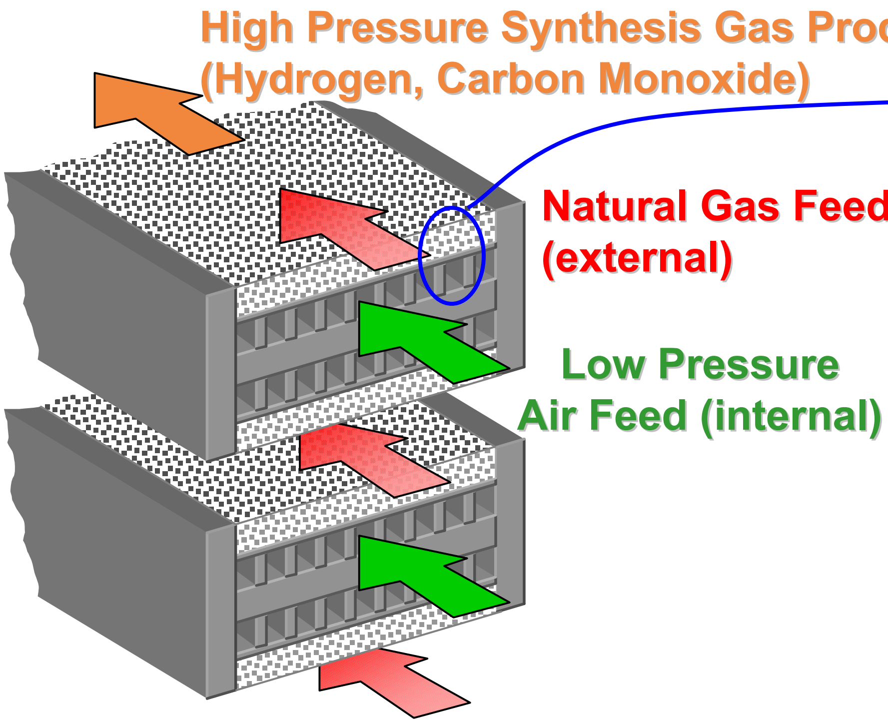
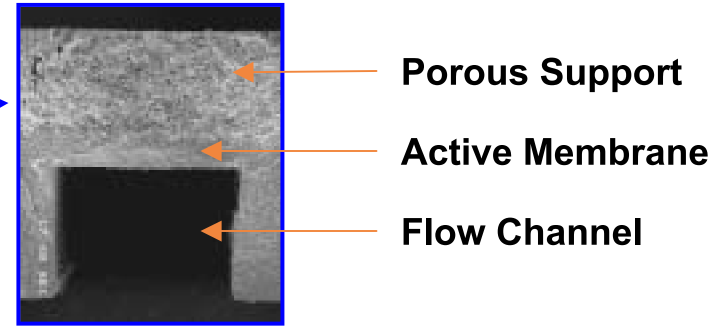
Technical Accomplishments
Advanced Planar Ceramic Membrane



Ceramic Wafer Stack Diagram



Multi-membrane Module with Hermetic All-Ceramic Joints

- Compact, *microchannel* design
- *All-ceramic joints* have been demonstrated for assembly of single membranes into a module and have significant benefits
  - Uniform materials to match expansion behavior and reduce stress
  - Key enabling technology

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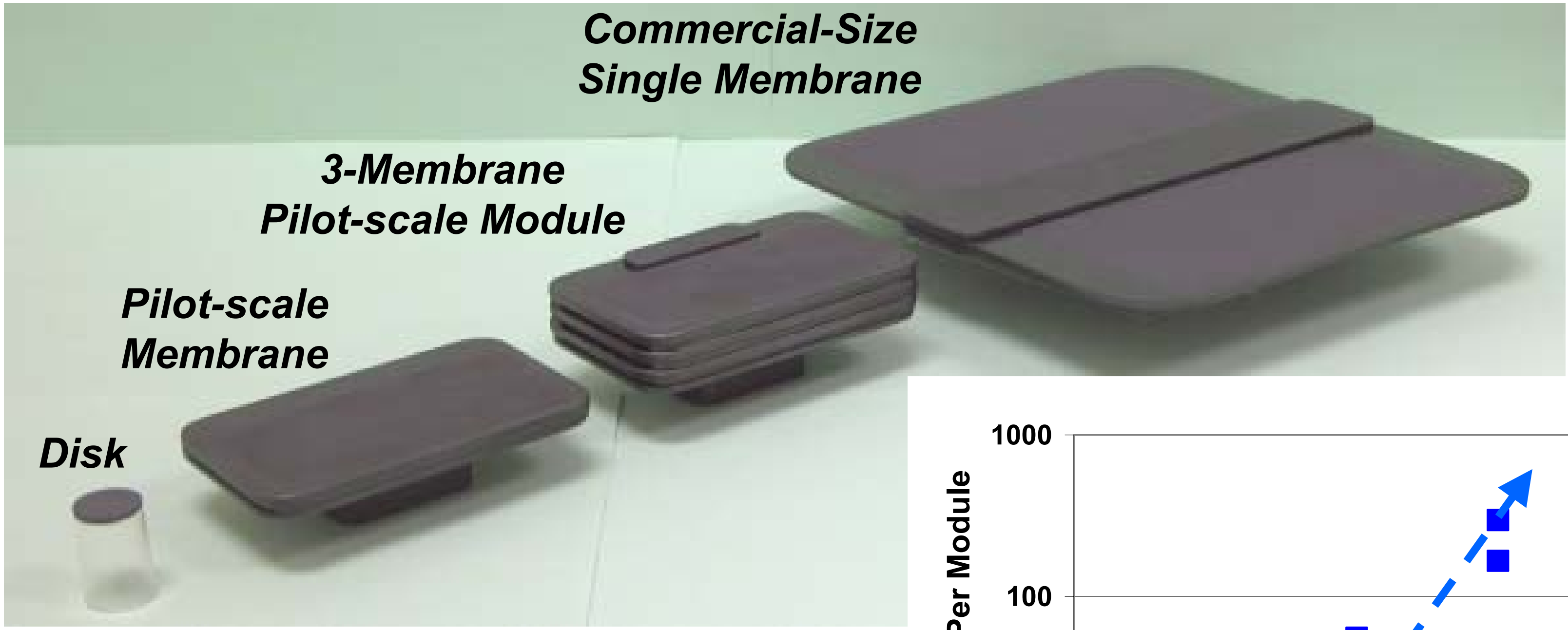
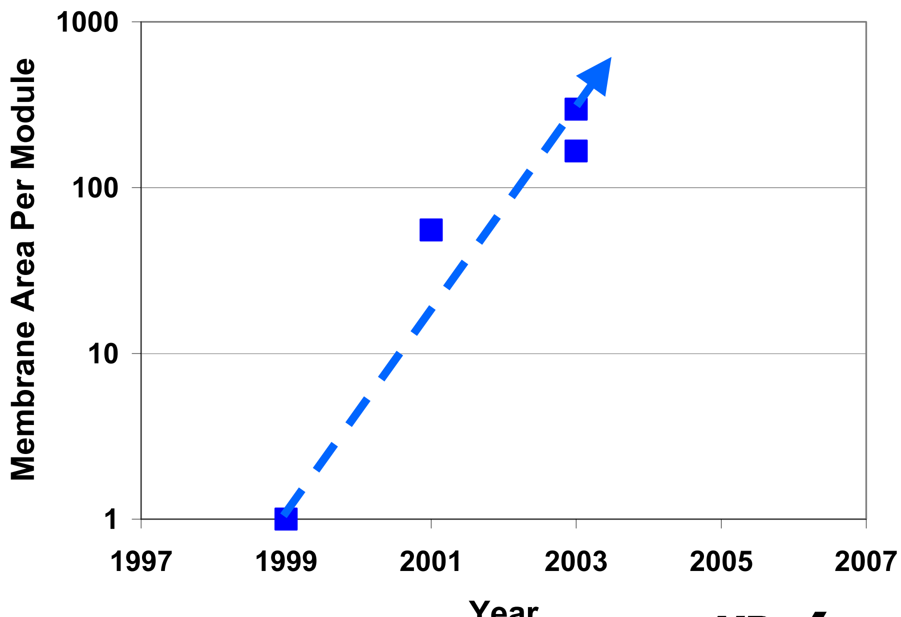
Technical Accomplishments
Rapid Advance in Ceramic Module Fabrication



- Factor of 300 increase in module area since 1999
- Internal structures of commercial membrane tested in pilot-scale membrane
- Scalable ceramic processing methods



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Technical Accomplishments

ITM Syngas Membrane Materials Meet Severe Demands

- Patented composition
  - $(La_{1-x}Ca_x)_yFeO_{3-\delta}$ where $0<x<0.5$ and $1.0<y$
- Thermodynamic stability in different environments
  - High-pressure, reducing environment on the natural gas side
  - Low-pressure, oxidizing environment on the air side
- Electronic and oxygen ion conductivity to achieve economically attractive oxygen flux
- Mechanical properties to meet lifetime and reliability criteria

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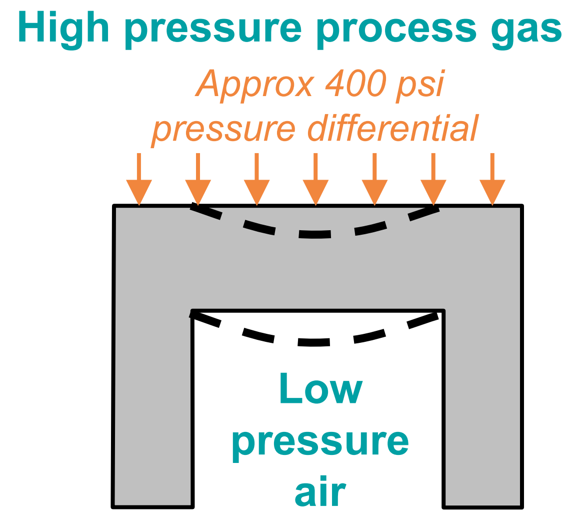
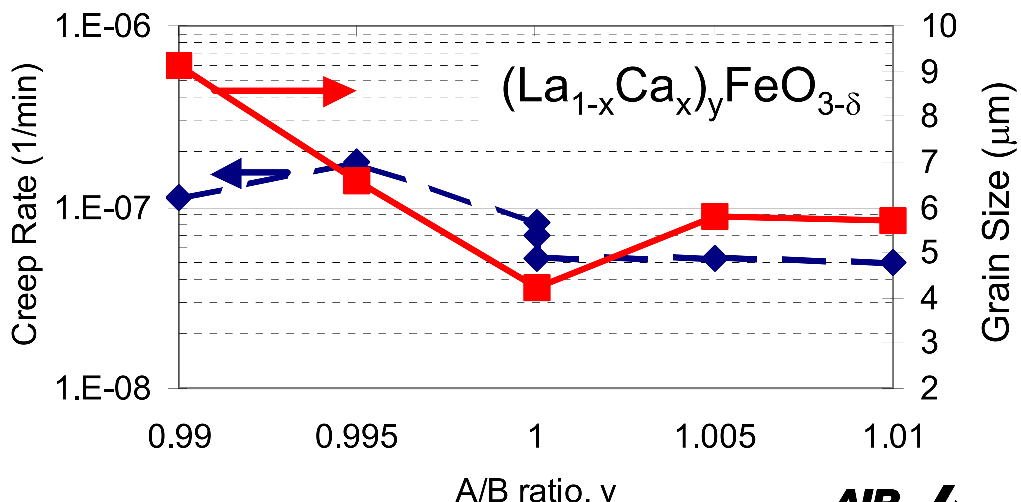
Technical Accomplishments

Membrane Materials and Structures Are Creep Resistant

- Operation with high pressure natural gas and low pressure air is preferred
  - Results in capital and operating cost savings
- Membrane microchannel structure supports approximately 400 psi pressure differential
- ITM Syngas membrane materials are tailored to meet creep requirements to achieve long service life
  - Maintaining A/B cation ratio (y) greater than 1.0 decreases creep rate by a factor of 2 or greater

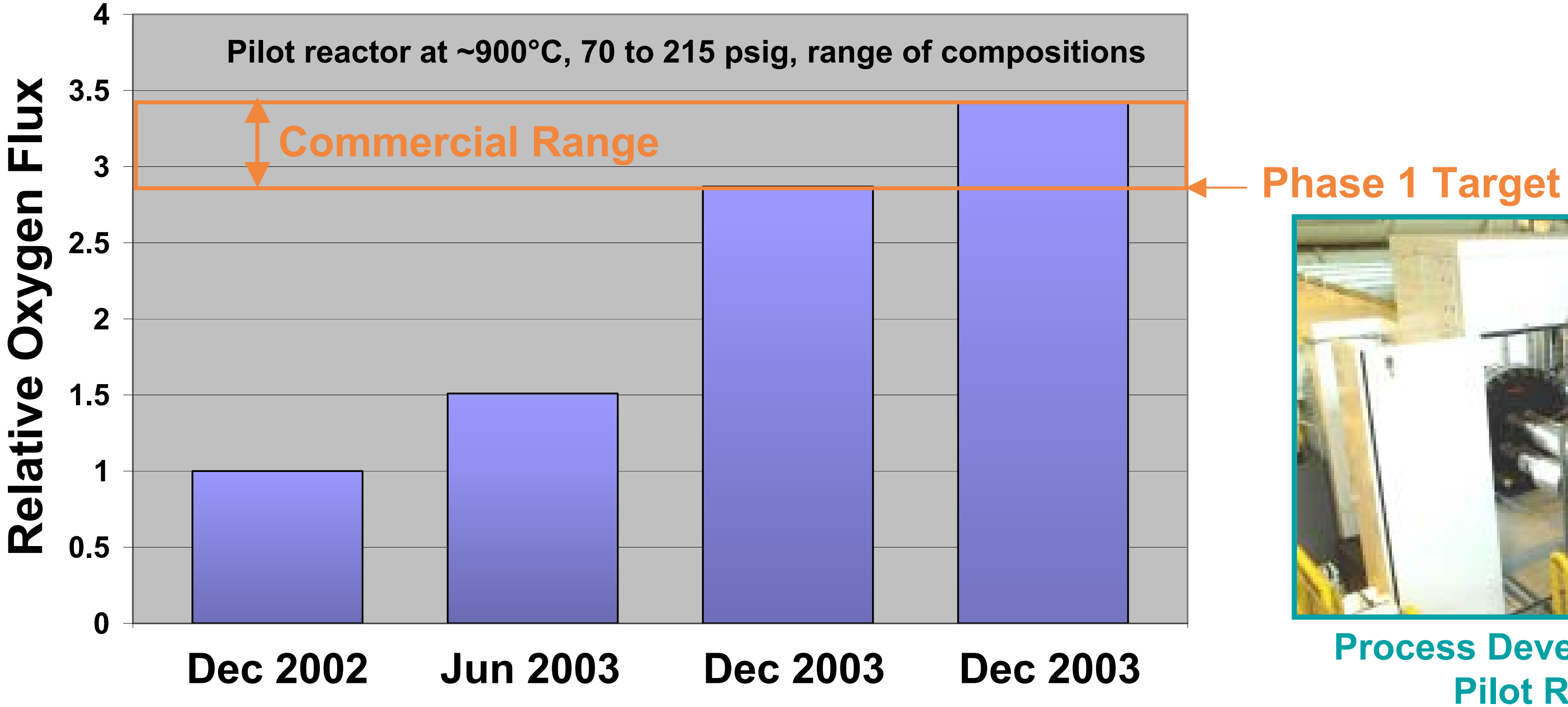


ITM Syngas Microchannel Structure



Technical Accomplishments

Target Fluxes Demonstrated in Pilot Reactor



Process Development Unit
Pilot Reactor

- Pilot-scale Process Development Unit (PDU) demonstrated *design capacity and target flux* in FY2004
- *Over factor of 3 increase* in measured flux since 2002
- *Improvements* in membrane design, reactor design, and operation
- Pilot-scale membranes have been *operated* at commercial process conditions *and survive* changes in operating conditions

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Interactions and Collaborations

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ChevronTexaco
U.S. DEPT. OF ENERGY
ceramatec
ELTRON RESEARCH
SOFCo
University of Pennsylvania
University of Alaska Fairbanks
PENNSTATE

- **Broad team includes industry and universities**
- **FY2004 Publications and Conferences**
  - **"*Development of the ITM Syngas Ceramic Membrane Technology*," AIChE Spring National Meeting, New Orleans, April 26, 2004.**
  - **"*ITM Syngas Ceramic Membrane Technology for Synthesis Gas Production*," 7th Natural Gas Conversion Symposium, Dalian, China, June 6-10, 2004.**
  - **"*Hydrogen and Syngas Production Using Ion Transport Membranes*," 8th International Conference on Inorganic Membranes, Cincinnati, OH, July 18-21, 2004**

Response to 2003 Reviewers' Comments

- "*This project is very critical to realizing the hydrogen economy*"
- "*Needs to address natural gas pre-treatment, performance, and wafer stability. There are issues with contaminants.*"
  - Process designs and costs include natural gas pre-treatment (e.g. desulfurization, pre-reforming)
  - Since 2001, flux stability has improved by a factor of over 25 and several long-tem tests meet flux stability target
  - Improved designs in pilot reactor have dramatically reduced contaminants from process system materials of construction
- "*Emphasize higher pressure and higher temperature testing*"
  - Membranes operated in laboratory and PDU pilot reactors at commercial pressure and temperature (up to 425 psig and over 900 °C)

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Milestones and Future Work

- *Completed Milestones*
  - Demonstrated target performance of pilot-scale membrane at commercial process conditions and PDU design capacity
  - Fabricated multi-wafer module of pilot-scale membranes
  - Fabricated commercial-size planar membrane and prototype SEP module components
- *Remainder of FY2004*
  - Test catalyzed planar membranes in PDU
  - Initiate tests to validate commercial-size membrane design
- *FY2005*
  - Fabricate integrated sub-scale membrane module of commercial-size planar membrane
  - Test sub-scale module of commercial-size planar membrane
  - Demonstrate performance of commercial-size planar membrane which meets economic targets at commercial conditions
  - Initiate engineering design of the Sub-scale Engineering Prototype plant

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